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AUTOMATION OF AN ION CHROMATOGRAPH FOR PRECIPITATION ANALYSIS WITH COMPUTERIZED DATA REDUCTION

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Minimum limits of detection and quantitation for each anion are calculated; these limits are a function of suppressor exhaustion. Precision for replicate analyses of six precipitation samples for fluoride, chloride, orthophosphate, nitrate, and sulfate ranged from 0.003 to 0.027 milligrams per liter. To determine accuracy of results, the same samples were spiked with known concentrations of the above mentioned anions. Average recovery was 108 percent.

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By Arthur G. Hedley and Marvin J. Fishman

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations 81-78

Denver, Colorado
1982

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By

Arthur G. Hedley and Marvin J. Fishman

ABSTRACT

Interconnection of an ion chromatograph, an autosampler, and a computing integrator to form an analytical system for simultaneous determination of fluoride, chloride, orthophosphate, bromide, nitrate, and sulfate in precipitation samples is described. Computer programs provided with the integrator are modified to implement ion-chromatographic data reduction and data storage. The liquid-flow scheme for the ion chromatograph is changed by addition of a second suppressor column for greater analytical capacity. An additional valve enables selection of either suppressor column for analysis, as the other column is regenerated and stabilized with concentrated eluent.

Minimum limits of detection and quantitation for each anion are calculated; these limits are a function of suppressor exhaustion. Precision for replicate analyses of six precipitation samples for fluoride, chloride, orthophosphate, nitrate, and sulfate ranged from 0.003 to 0.027 milligrams per liter. To determine accuracy of results, the same samples were spiked with known concentrations of the above mentioned anions. Average recovery was 108 percent.

INTRODUCTION

This paper describes the interconnection of an ion chromatograph, autosampler, and computing integrator to form an analytical system for the simultaneous, rapid, and unattended analysis of precipitation samples for major inorganic-anion constituents. Chromatographic data are reduced at the analyst's convenience with a minimal amount of input. Precision and accuracy data also are presented.

Ion chromatography is a combination of ion exchange, eluent suppression, and conductimetric detection. A sample is injected into a liquid mobile phase being pumped through two ion-exchange columns placed in series. In the first column, called the separator, anions (in this method) are separated on the basis of their affinity for exchange sites in the resin. The second column, called the suppressor, decreases background conductivity of the mobile phase, called the eluent, to a minimal level, and converts the anions in the sample to their corresponding acids. Separated anions in their acid form are quantitated with a specific conductance cell. For further details on the principles, see Small, Stevens, and Bauman (1975).

Ion chromatography is a useful tool for determining anions in precipitation samples. Detection limits for many of the anions are lower when ion chromatography is used rather than other techniques, and several anions are determined sequentially using only a small aliquot of particulate-free sample.

Use of ion chromatography in a manual mode, as applied to the analysis of precipitation samples, appears in several publications (Fishman and Pyen, 1979; Bogen and Nagourney, 1979; Tyree, Stouffer, and Bollinger, 1979). Adaptation of an ion chromatograph to microprocessor control for the analysis of rainwater, and programs for peak detection are described by Slanina and others, (1979). Each analysis takes about 50 min (minutes), however.

EXPERIMENTAL DESIGN

Apparatus

Ion Chromatograph

A Dionex Model 10[1/] is used throughout the study; its flow diagram is shown in figure 1. Modification is required to automate the system; to partly accomplish this modification, the sample injection valve 7 is bypassed. Details of the modification are discussed later.

Autosampler

A Micromeritics Model 725 is used to automate the sample processing. A length of standard PTFE (polytetrafluorethylene) tubing 0.8 mm (millimeter) I.D. (inside diameter) X 1.5 mm O.D. (outside diameter) having a volume of 600 uL (microliters) is substituted for the stainless steel sample loop supplied with the autosampler. A "reverse sampling board" is used instead of the "normal sampling board." This allows the sample loop to be both rinsed and filled with the maximum available sample vial volume of 730 uL.

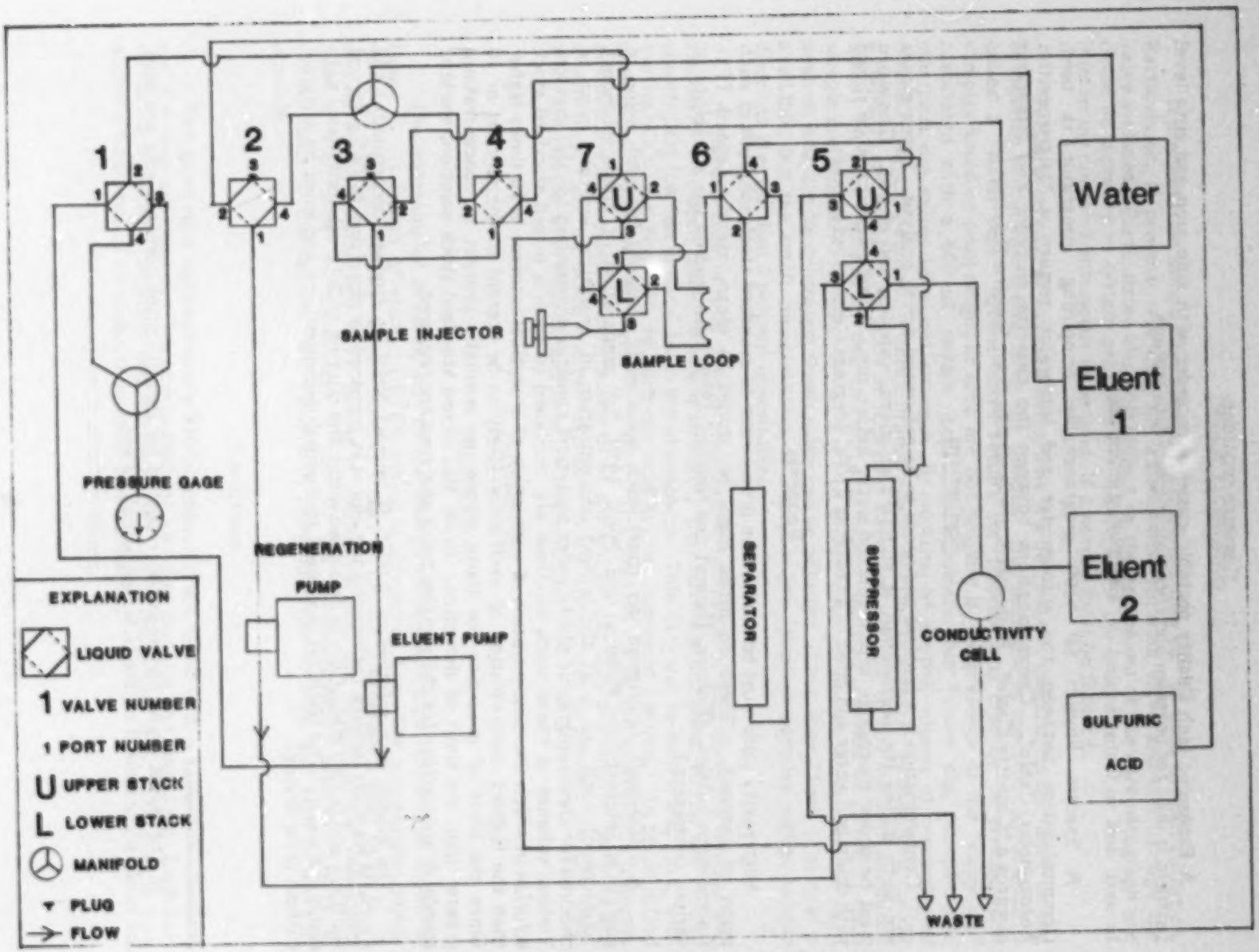

Figure 1. Ion chromatograph flow diagram.

Cassette recorder

A Panasonic high fidelity portable cassette recorder with auto stop and auto level features is used for program and chromatographic-data storage.

Computing integrator

A Spectra Physics SP 4100 programmable computing integrator is used. Communications between the autosampler and integrator require a "Micromeritics Autosampler Cable". Communications between the cassette recorder and integrator requires a "Cassette Cable". Both cables are available from Spectra Physics.

Precautions

Contamination is a problem and needs to be prevented during analysis. Latex gloves are worn during the preparation of standard solutions, samples, and eluent. Glassware must be rinsed thoroughly with deionized water before use. Sample vials must be rinsed with deionized water and dried in an oven at 110°C (degrees Celsius) before use.

Reagents

High purity salts must be used in the preparation of standard stock solutions of each anion of interest. These solutions must be stored in clean, tightly capped TFE-fluorocarbon bottles. (Fulmer, Penkrot and Nadalin, 1979, have studied the suitability of various containers.)

A 1,000-mg/L (milligram per liter) stock solution is prepared for each anion of analytical interest (see Fishman and Pyen, 1979, for preparation of stock solutions). Solutions of each anion, at the highest concentration of analytical interest, must be checked for chromatographic purity under analytical conditions described for this method. Various volumes of these stock solutions are combined to form a mixed standard stock solution in which the concentration of each anion of analytical interest is 10 times higher than the highest concentration of each anion likely to be present in the sample, or 10 times the limit of detection for those anions not normally present in concentrations greater than the limit of detection. From this mixed standard stock solution, working standards appropriate for the samples being analyzed are prepared.

The eluent is a solution of 0.0030 M (molar) $NaHCO_3$ (sodium bicarbonate) and 0.0024 M Na_2CO_3 (sodium carbonate); the eluent is prepared by dissolving 0.5040 g (gram) $NaHCO_3$ and 0.5088 g Na_2CO_3 in deionized water and diluting to 2000 mL (milliliters) with deionized water. The $NaHCO_3$ is subject to thermal decomposition and must be weighed without prior drying.

1/ The use of brand names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

Sample Preparation

If precipitation samples are free of particulates, they can be used without filtration. Particulates, if present, will clog the autosampler rotating valve and can damage the valve surfaces. Particulates also will collect on the precolumn of the chromatograph and cause an increase in system pressure. A filter 0.045 um (micrometer) or less free of interfering contaminants needs to be used if a sample must be filtered.

A characteristic of ion chromatograms is a decrease in specific conductance caused by dilution of the eluent stream by the sample. This decrease in specific conductance is called a "water dip." Quantitative results for fluoride and chloride in precipitation samples based on peak height or area are not possible in the presence of the "water dip" associated with a 600 uL sample loop. To eliminate this "water dip," samples and standards are spiked to eluent strength by addition of a small volume of concentrated $NaHCO_3/Na_2CO_3$ eluent. A concentrated eluent solution is prepared by dissolving 0.6552 g $NaHCO_3$ and 0.6614 g Na_2CO_3 in deionized water and diluting to 100 mL with deionized water. A 1 mL volume of this concentrated eluent solution is added to 25 mL of each sample and standard. A minimum of 2 mL of eluent strength sample is required for each analysis and the concentrated eluent spike can be adjusted, if less than 25 mL of sample is available, but the small concentration of anions in precipitation samples makes sample dilutions greater than 5 percent undesirable.

A disadvantage of this sample preparation technique is that once the samples and standards have been spiked to eluent strength, they have a pH of about 10 and will readily absorb CO_2 (carbon dioxide) from the atmosphere. This CO_2 will be converted, along with the $NaHCO_3$ and Na_2CO_3, to carbonic acid in the suppressor column. An unidentified peak in the region of the "water dip", that shifts position during the suppressor's lifetime, is indicative of unequal concentrations of eluent and sample CO_2 absorbtion. Samples and eluent must have the same minimal exposure to the atmosphere to prevent the CO_2 peak from interfering with fluoride and chloride quantitation.

Autosampler

Modifications

The autosampler is connected to the ion chromatograph flow scheme as shown in figure 2. A length of standard PTFE tubing is connected from the autosampler check valve port labeled "PUMP" to the number 2 port of the chromatograph's gage valve 1. A second length of standard PTFE tubing is connected from the sampler check valve port labeled "COLUMN" to the number 1 port of the chromatograph's separator valve 6. Connections to the sampler are made with Swegelok-type fittings, and kept as short as possible.

Conditions

Two glass vials (approximately 950-uL capacity) are filled with a sample or standard and the vials are capped. This is repeated for all other samples and standards. Each pair of vials are placed in adjacent odd and even positions of the sample tray. The sample tray allows a maximum of 64 vials (32 samples and standards).

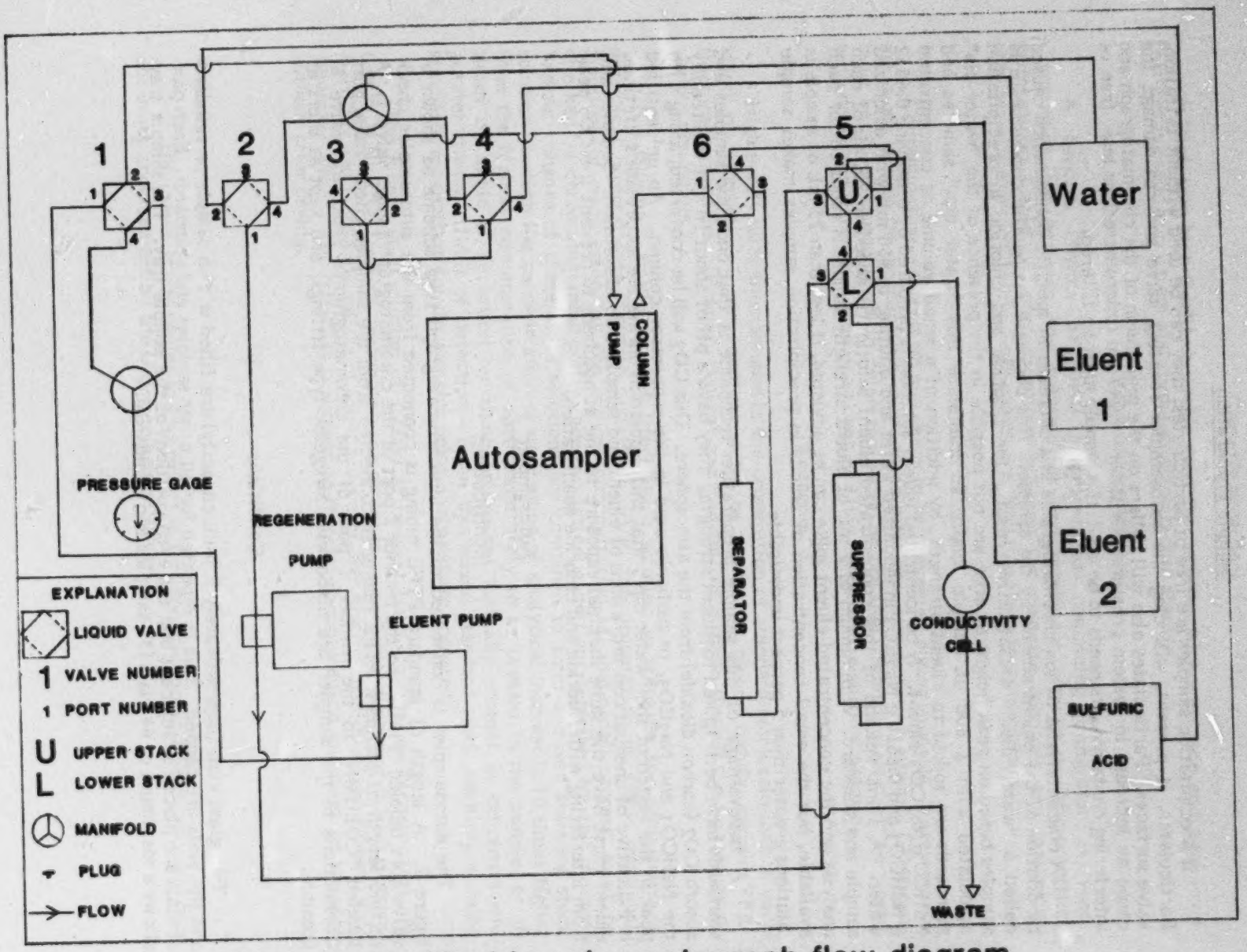

Figure 2. Modified ion chromatograph flow diagram.

The autosampler is turned on, and, with the sample loop in the chromatograph's eluent flow path, the chromatograph's eluent pump is adjusted to the flow rate described under the section on chromatographic conditions. The autosampler's "RINSES" control is set at "ODD". This permits the sample loop to be rinsed with a vial delivery volume of 730 uL from each vial in an odd numbered position, and filled from each vial in an even numbered position.

With the "reverse sampling board" installed, the "INJECTIONS PER VIAL" control is set at 1. The "MINUTES PER INJECTION" thumbwheel is set to have the sampler advance to the next sample about 1 min after the last peak of the chromatogram has integrated and baseline has been reestablished. The "LAST SAMPLE" thumbwheel is set to coincide with the last occupied sample tray-position (64 when a full tray is being used).

Ion Chromatograph

Conditions

Chromatographic separation of the anions is achieved by use of a standard, plastic anion-separator column (Dionex No. 30827 or equivalent) that has been shortened by cutting off about 10 cm (centimeters) with a tubing cutter and reattaching the end fitting. The purpose of shortening the separator column is to minimize the time required for each analysis while retaining sufficient resolution for accurate quantitation of the anions of interest (fluoride, chloride, orthophosphate, bromide, nitrate, and sulfate). Eluent suppression is achieved by the use of an anion suppressor column packed with a high-capacity cation exchange resin (Dionex No. 30828 or equivalent), that is capable of converting the eluent and separated anions to their respective acid forms. A precolumn containing a low-capacity anion exchange resin (Dionex No. 30825 or equivalent) is used to protect the main separator column.

One of the factors limiting precision of this analytical system is the fact that response of the conductivity detector is a function of suppressor exhaustion (Fulmer, Penkrot, Nadalin, 1979). To provide a stable baseline, the suppressor is stabilized with eluent for 1 to 2 h (hours) before beginning a series of analyses. Here, stable is defined as a conductivity detector response variation of less than $\pm$ 20 uV/min (microvolts per minute). The stable lifetime of a suppressor is about 8 h under the conditions described for this method.

The chromatograph's eluent and regeneration pumps have a maximum flow rate of about 500 mL/h (milliliters per hour). A vernier on the pump allows adjustment of the flow rate from zero to 100 percent of maximum. The regeneration pump is set at 30 percent, and the eluent pump is set at about 30 percent, so mean system pressure for the latter pump is 500 lb/in^2 (pounds per square inch) (600 lb/in^2 maximum). The chromatograph's full-scale specific-conductance setting is 300 umho/cm (micromhos per centimeter at 25^0C).

Exceeding the range of the conductivity meter for a long time will damage the power supply of the conductivity-detector circuit. This situation occurs when the suppressor is exhausted, and unsuppressed eluent is allowed to flow through the conductivity cell. The chromatograph must be powered from the autosampler's 110-volt utility outlet, when operating unattended. This allows the autosampler to turn off the chromatograph after the last sample is analyzed and before total suppressor exhaustion.

Modifications to increase analyzing capacity

The most time-consuming aspect of this system, as mentioned, is the 1 to 2 h required to regenerate and stabilize the suppressor column. To improve the efficiency of the system, the ion chromatograph was replumbed and fitted with an additional suppressor valve and suppressor column. The flow diagram for the replumbed chromatograph is shown in figure 3. Air lines to the former gage valve 1 (fig. 1 and 2) have been connected to the new suppressor type valve 8. Valve 8 allows the analyst to switch back and forth between the two suppressor columns. When the former gage valve air actuator toggle is in the "ON" position, suppressor 1 is in the analytical part of the flow system. When the toggle is in the "OFF" position, suppressor 2 is in the analytical part.

The suppressor that is not in the analytical part of the flow system is in a regeneration and stabilization part of the flow system. To construct this part of the system, the former injection valve (no longer in use) is modified. A diagram of the original injection valve 7 is shown in figure 4. The injection valve is a four-way valve in the "LOAD" position, but a two-way valve in the "INJECT" position. The modified version of the injection valve 7m also is shown in figure 4. The upper stack of the original injection valve is replaced by gage valve 1. The pressure gage becomes a permanent part of the flow system. This modified valve 7m permits a suppressor to be regenerated in the usual way, when the former injection valve air actuator toggle is in the "LOAD" position. Once the rinse cycle is finished, the "RGN" timer is set to zero and the "RIN" timer is set to 60 min. With the modified injection valve air actuator toggle in the "INJECT" position, initiating the regeneration cycle causes eluent in the stabilizer reservoir to be pumped through the suppressor. For more rapid stabilization, a concentrated Na_2CO_3 solution can be used in the stabilizer reservoir.

All connections are made with PTFE tubing (0.8 mm I.D. X 1.5 mm O.D.), except the line from the stabilizer reservoir, which is 1.5 mm I.D. X 3.0 mm O.D. PTFE tubing. The waste line from port 3 of the upper stack of the former injection valve is reconnected to port 3 of the upper stack of the modified injection valve, 7m.

Computing Integrator

Conditions

The ion chromatograph's 0 to 1 volt output is connected directly to the integrator's input contacts. The integrator's internal range selection switch is set at 1 volt. In this range, the integrator has a resolution of 0.5 uV·s/c (microvolt-second per count) and a maximum peak area capacity of 10^9 uV·s.

The computing integrator is leveled at 10 mV (millivolts). Chart speed is at the default value of 1 cm/min (centimeter per minute), and the attenuation is set at 16. Time function "PM1" is actuated to provide peak markers, and time function "NE1" is actuated to prevent printing of time function occurrences on the chromatogram. Report parameter "PH" is set equal to 2. This causes storage of both peak height and area data for each chromatogram.

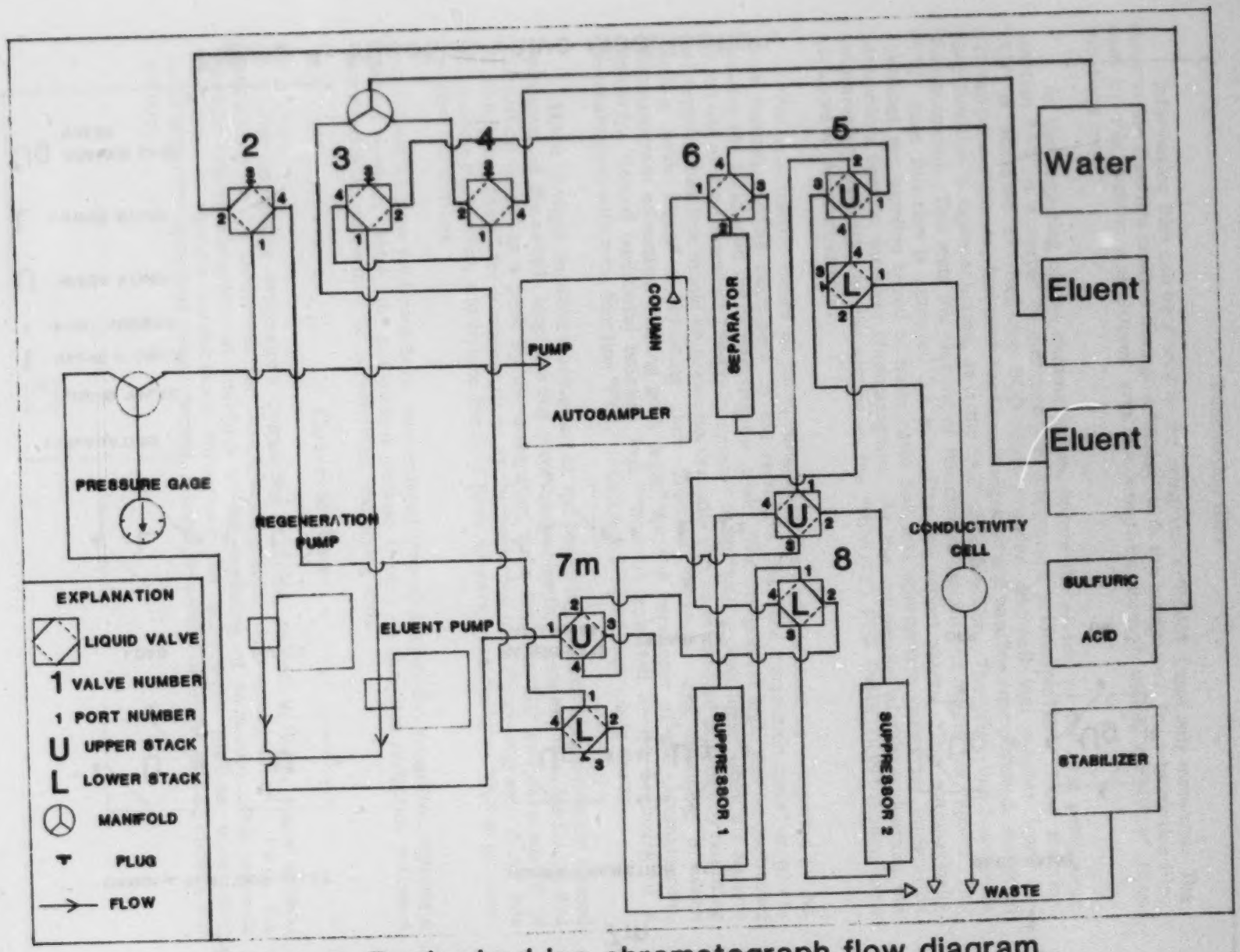

Figure 3. Replumbed ion chromatograph flow diagram.

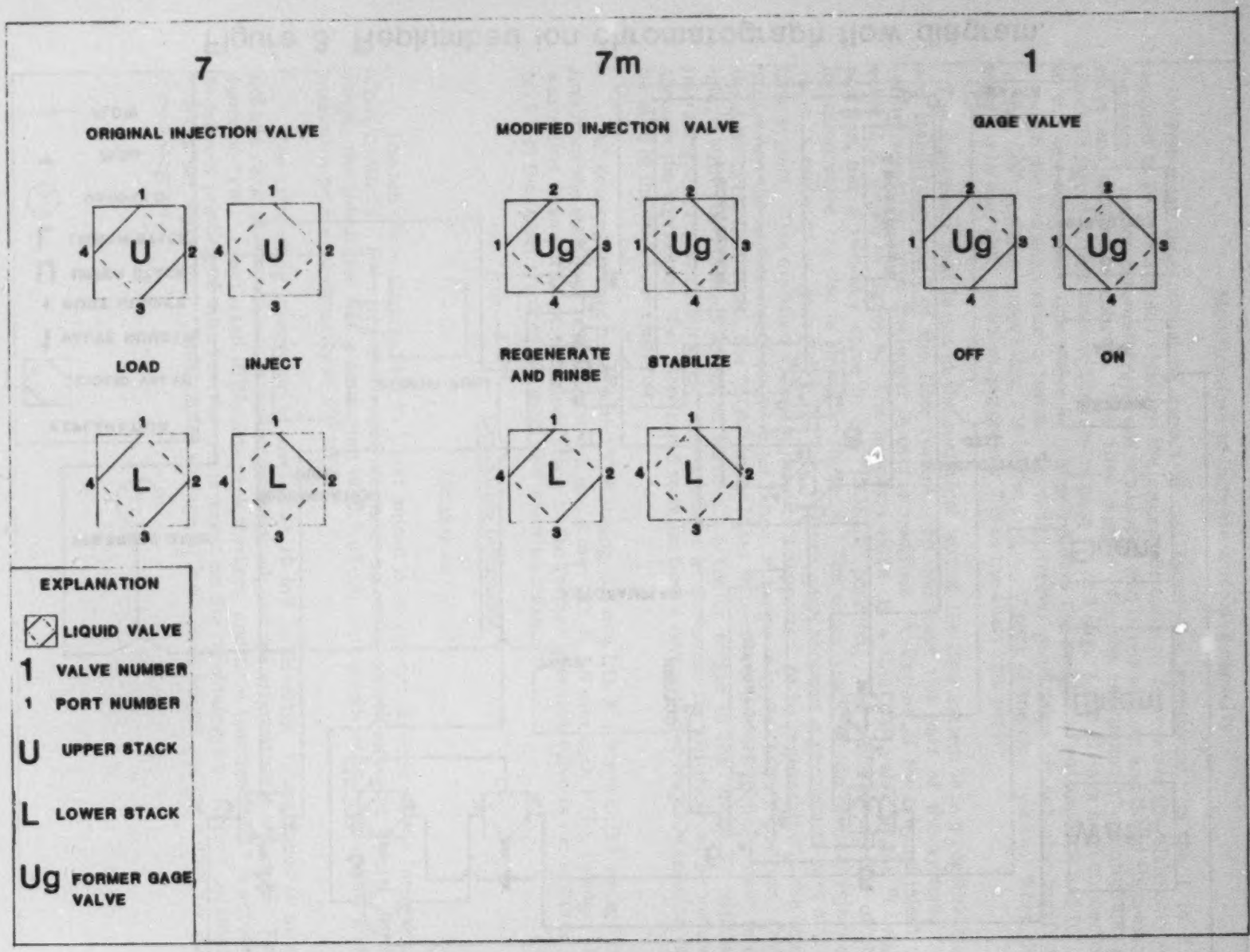

Figure 4. Injection valve modification.

Information files

Information files can be stored in the integrator's "ROM" (read only memory). The information files are created through a "dialog" with the integrator. The information files used by this system, and entered into the integrator through dialog, consist of time functions only.

At the beginning of the chromatogram, before the elution of the first peak, time function "AZ" is actuated to autozero the integrator's printer/plotter. Time function "XD" is actuated to read the BCD (binary coded decimal) vial number from the autosampler. After the last peak has been integrated and baseline reestablished, the "XD" time function is again actuated, as is the "AZ" time function. The "ER" time function is then actuated. This ends the plotting of the chromatogram and begins the report. The "ET1" time function is actuated 0.2 min after the report starts. This automatically evaluates the baseline signal to noise ratio and sets appropriate values for integration parameters used in the next chromatogram. At the completion of this evaluation, the autosampler, controlled by the setting on the "MINUTES PER INJECTION" thumbwheel, advances to the next sample.

For quantitation based on area, samples and standards must be integrated in the same manner. After each peak in the report, a "baseline correction code" is given, showing the logic used for integrating the peak. The integration logic can be controlled by the use of time functions. Peaks integrated using "tailing peak logic" when the analyst believes the baseline should be drawn horizontally can be integrated properly by not using "tailing peak logic." Actuating time function "TP1" at the beginning of each chromatogram eliminates "tailing peak logic" for the remainder of the chromatogram. Similarly, "forced horizontal baseline logic" may be actuated at the beginning of a chromatogram with time function "FH1," if baseline is being improperly drawn.

There is slight baseline fluctuation at the beginning of each chromatogram caused by reentry of the sample loop into the chromatograph's flow system. To avoid having this fluctuation "seen" as a peak by the integrator, time function "II1" can be actuated to "inhibit integration" for a minute or so at the beginning of a chromatogram. After this fluctuation has passed, and before the first peak appears, time function "IIØ" is actuated to allow integration.

When all time functions have been entered through dialog, the integrator requests a method number. Here, the calculation method is part of the data reduction software described later, so method "0" is requested, and dialog ends.

Custom Software

The computing integrator's calculating routines, stored in ROM, place several restrictions on its usefulness for ion-chromatographic data manipulation. First, the routines require placement of standards at the beginning of each run. This prevents variations in specific conductance throughout the suppressor's lifetime from being reflected in the analytical curve. Second, a linear or second order fit may be chosen, but not both.

Calculations normally are based on a linear fit, but information derived from fitting a parabola to the data is useful. (See Discussion). Third, anion concentrations can be calculated on the basis of peak area or peak height, but not both. If an interference is present as an unresolved shoulder, the concentration calculation based on area may be in serious error, but a calculation based on height would give acceptable results. Fourth, standards must not contain anions of interest with concentrations that result in peak areas greater than 999,999 uV·s, or the analytical curve cannot be constructed due to numerical overflow.

The computing integrator's "ROM"-based calculating routines can be reprogrammed into the "RAM" (read/write memory) part of the integrator's memory, and modified to fit specific analytical needs. This provides the analyst with a more versatile system resulting in a wider range of options for processing the data generated by a series of chromatograms.

Data acquisition software.--A listing of program "AUTPART1" is shown in table 1. The program is loaded into the integrator's "RAM" from the cassette recorder before beginning a series of chromatograms. Only one program variable must be initialized at the beginning of a series of chromatograms: Cc is set equal to 1. Standards can be placed in any order, and anywhere in the sample tray. Generally, they are dispersed throughout the samples. As a series of chromatograms are obtained, the integrator prints two reports for each chromatogram. The first report contains peak-area information, and the second contains peak-height information. Data contained in each report are stored in the computing integrator's "RAM". As many as 254 sets of peak data can be stored in a file.

Beginning Analysis

When the suppressor is stable, autosampler loaded and all controls set, integrator dialog entered, and program "AUTPART1" loaded into the integrator's RAM, then the signal-to-noise ratio for the first chromatogram is evaluated. After the integrator finishes the evaluation, the autosampler "RUN" button is pushed to start the series of analyses. The system can be left unattended.

Data-Storage and Retrieval Software

At the end of a series of chromatograms, program statement 200 is executed. The printer will then print a unique number identifying each peak, followed by the vital data associated with each peak.

A listing of program "DATASAVE" is shown in table 2. This program is a slightly modified version of a program used for data logging and is discussed at length in the manufacturer's manual. This program permits cassette storage of data necessary for the curve-fitting program "AUTPART2" and also allows reloading of chromatogram data from the cassette into the integrator's "RAM".

Table 1.--Listing of program "AUTPART1"

```
 19 REM "AUTPART1"
 20 REM Cn= THE NUMBER OF CHROMATOGRAMS.
 22 REM Np(Cn)= THE NUMBER OF PEAKS IN CHROMATOGRAM Cn
 24 REM Tp= THE TOTAL NUMBER OF PEAKS IN ALL CHROMATOGRAMS.
 26 REM Pa(I)= THE AREA OF PEAK I.
 28 REM Ph(I)= THE HEIGHT OF PEAK I.
 30 REM Pt(I)= THE RETENTION TIME OF PEAK I.
 32 REM Bc(I)= THE BASELINE CORRECTION CODE FOR PEAK I.
 36 REM AFTER ENTERING THE PROGRAM, INITIALIZE PH=2, Cc=1.
 38 REM RECORD THE CHROMATOGRAMS AS USUAL. THE PROGRAM
 40 REM IS ACCESSED THROUGH A ROM PATCH AT LINE 4840.
 42 REM A REPORT OF PEAK HEIGHTS AND AREAS FOLLOWS EACH
 44 REM CHROMATOGRAM IN ADDITION TO STORING THE DATA.
 50 IF Cc=0 THEN 70
 60 Aa=0: Bb=0: Cn=0: Tp=0: Ii=0
 65 Cc=0
 70 J=0: IF PH=1 THEN 110
 85 Aa=Tp+1: Bb=Tp+Z: FOR I=AaTO Bb: J=J+1: Pt(I)=PST(J)
 90 Pa(I)=PSA(J): Bc(I)=PSF(J): NEXT
100 PH=1: GO TO 2070
110 FOR I=Aa TO Bb: J=J+1: Ph(I)=PSA(J): NEXT
115 REM SET USER VARIABLES FOR NEXT RUN. RETURN TO ROM.
120 PH=2: Cn=Cn+1: Np(Cn)=Z: Tp=Tp+Z: GO TO 4850
130 REM THIS PART OF THE PROGRAM WILL
135 REM DISPLAY THE DATA ACCUMULATED AT THE END OF A
140 REM SERIES OF CHROMATOGRAPHIC RUNS.
150 REM TO DISPLAY THE DATA ENTER RUN 200
200 !"PEAK#";TAB10"RT";TAB23"AREA";
205 !TAB11"PK HT";TAB21"BC"
210 K=1: FOR J=1 TO Cn: I=1
215 !TAB11"CHROMATOGRAM#";$2J;
220 !TAB15"NUMBER OF PEAKS";$3Np(J)
225 !$3K, $5.3Pt(K), $10Pa(K), $10Ph(K), $2.04Bc(K)
230 I=I+1: K=K+1: IF I<=Np(J) THEN 225 ELSE NEXT : END
4830 ECH01
4840 !!: PLOT 0
4841 POKE #C2CD,0: DISP
4842 GO TO 50
```

Table 2.--Listing of program "DATASAVE"

```
298 REM PROGRAM 'DATASAVE'.  START RECORDING.  ENTER RUN 300.
299 REM SAVES TIMES, HEIGHTS, AREAS, CORRECTION CODE.
300 POKE #8C107,8: DV=2: POKE #C388,PEEK#C387
305 !''''''''''''''''
310 !Tp
315 FOR K=1 TO Tp
320 !Pt(K),Pa(K),Ph(K),Bc(K)
325 NEXT
330 !''''''''''''''''
335 DV=1: !'DONE'
340 POKE #8C107,0
345 END
399 REM
400 POKE #8C107,8: POKE #C388,PEEK#C387
405 BAUD 300
410 !'READY FOR DATA'
415 DV=2: ECHO 0
420 INPUT ''Tp
425 IF RXD<>16 THEN 420
430 LEDS Tp,
435 FOR K=1 TO Tp
440 INPUT ''Pt(K),Pa(K),Ph(K),Bc(K)
445 LEDS K,
450 NEXT
455 DV=1: GOTO 460
460 LEDS 'END DATA'
465 END
466 REM
2056 BAUD 2400: STOP : REM 'SLOPE' instead of 'ESC'
```

Data-Reduction Software

A listing of program "AUTPART2" is shown in table 3. This program uses the data from "AUTPART1", or loaded from cassette, to fit the standards to both a linear and non-linear working curve. Constants required by program "AUTPART3" and "AUTPART4" are calculated and stored in the integrator's "RAM". The output printed by program "AUTPART2" provides information about how well the standards fit linear and parabolic curves. Use of the information is explained in the discussion. An example of the output generated by "AUTPART2" is shown in figure 5.

A listing of program "AUTPART3" is shown in table 4. This program calculates the concentration of each anion in each sample. A concentration based on both peak height and peak area is calculated, and a difference of more than 10 percent between the two results causes a flag (**) to be printed. Flags usually indicate values less than the limit of quantitation of the method or a suspect concentration based on the area of a peak that includes an unresolved shoulder interference.

A listing of program "AUTPART4" is shown in table 5. "AUTPART4" calculates an "expected limit of detection" and "expected limit of quantitation" in the following manner. Lines are constructed from each data point of an anion's calibration curve, to the mean of the calibration curve's data points. Linear error bounds are calculated as shown below. "AUTPART4" calculates, through an iterative process, the minimum concentration at which a 100 percent relative error can be expected. This is the "expected limit of detection." The minimum concentration at which a 10 percent relative error can be expected also is calculated, called the "expected limit of quantitation". The "expected "limit of detection" and "expected limit of quantitation" for each anion of interest, based on a typical set of standards, and calculated as described above, is shown in table 6.

The slopes of the error bounds are:

$$\text{slope} = m \pm ts\sqrt{n-1}$$

where

m = slope of the least squares best fit calibration line,

t = confidence coefficient of the students' t distribution for degrees of freedom n-1, and a confidence level determined by the analyst (generally the 95-percent confidence level is used),

s = standard deviation of the slopes of the lines from each data point to the mean of the data points, and

n = number of data points used in calculating s.

Table 3.--Listing of program"AUTPART2"

```
470 REM 'AUTPART2'
472 REM THE SECOND PART OF THIS PROGRAM IS DESIGNED TO
474 REM CONSTRUCT LINEAR AND NONLINEAR CALIBRATION
475 REM CURVES BASED ON BOTH AREA AND HEIGHT FOR EACH
476 REM ANALYTE. THE STANDARDS COULD HAVE BEEN PLACED
478 REM IN ANY ORDER.
480 REM BEFOR RUNNING THIS PROGRAM, THREE DATA LINES
481 REM MUST BE ENTERED.
482 REM THE FIRST DATA LINE HAS A FIVE CHARACTER
483 REM DISCRIPTION OF THE ANALYTE, AND THE NUMBER OF
484 REM DATA PAIRS FOR THAT ANALYTE'S CALIBRATION CURVE.
485 REM THE SECOND DATA LINE HAS THE CONCENTRATION OF
486 REM EACH DATA PAIR TO BE USED IN THE CALIBRATION
487 REM CURVE.
488 REM THE THIRD DATA LINE HAS THE PEAK NUMBER CORRES-
489 REM PONDING TO THE AREA THAT IS TO BE PAIRED WITH
490 REM THE CORRESPONDING CONCENTRATION IN LINE TWO.
491 REM FOLLOWING THE LAST PEAK NUMBER COMES A SCALING
492 REM FACTOR FOR THE AREA, FOLLOWED BY A SCALING
493 REM FACTOR FOR THE HEIGHT. A CURVE CAN NOT BE
494 REM CALCULATED FROM AREAS OR HEIGHTS LARGER THEN
495 REM 999.999.
496 REM AN EXAMPLE OF THE DATA LINES IS:
497 REM 800 DATA 'SO4-2',3
498 REM 810 DATA 2,4,6
499 REM 820 DATA 4,8,12,10,1
500 RESTORE 800: Ii=Ii+1: Z=1: READ An(Ii): READ N
505 RESTORE 810: FOR I=1 TO N: READ U(I): NEXT
510 RESTORE 820: FOR I=1 TO N: READ J
515 V(I)=Pa(J): W(I)=Ph(J): NEXT : READ Af(Ii): READ Hf(Ii)
520 FOR I=1 TO N: V(I)=V(I)/Af(Ii): W(I)=W(I)/Hf(Ii): NEXT
530 A=0: B=0: C=0: D=0: E=0: F=0: G=0: H=0: O=1: P=1
535 FOR I=1 TO N: X=U(I): IF Z=2 THEN V(I)=W(I)
540 Y=V(I): C=C+X: A=A+Y: D=D+Y*Y*Y: E=E+Y*X: O=O*X
545 P=P*Y: Y=Y*Y: B=B+Y: F=F+Y*Y: G=G+Y*X: H=H+X*X: NEXT
546 Kr(Ii)=C/N: Ks(Ii)=A/N: I=LOG O: I=I/N: Kt(Ii)=EXP I
548 I=LOG P: I=I/N: Ku(Ii)=EXP I
555 K=B*F: L=B*D: M=B*G: S=C*D: O=B*E: P=A*A: Q=B*B: R=D*D
560 J=(N*(K-R))+(2*A*L)-(P*F)-Q*B
565 T=N*(M-(E*D))+(A*(S+O))-(G*P)-(C*Q)
570 X=N*((E*F)-(D*G))+(A*(M-(C*F)))+(B*(S-O))
575 Y=(C*(K-R))+E*(L-(A*F))+G*((A*D)-Q)
580 IF J=0 THEN J=1
585 P=B-(P/N): IF P=0 THEN P=1
```

Table 3.--(Continued)

```
590 Ka(I:)=T/J: Kb(Ii)=X/J: Kc(Ii)=Y/J
595 Kd(Ii)=(E-(A*C/N))/P: Ke(Ii)=(C-(A*Kd(Ii)))/N
600 Ks(Ii)=(E-(C*A)/N)/(H-(C*C)/N)
602 Kh(Ii)=(A-(C*Ks(Ii)))/N
605 D=(H-(C*C)/N)/(N-1): D=SQR D
610 E=(B-(A*A)/N)/(N-1): E=SQR E
615 Kf(Ii)=Ks(Ii)*D/E
625 FOR I=1 TO N
630 F(I)=Ka(Ii)*V(I)*V(I)+Kb(Ii)*V(I)+Kc(Ii)
635 G(I)=F(I)-U(I): H(I)=100*G(I)/U(I)
640 K(I)=Kd(Ii)*V(I)+Ke(Ii)
645 L(I)=K(I)-U(I): M(I)=100*L(I)/U(I): NEXT
655 O="AREA": P=" HT ": Q=0: J=0: IF Z=2 THEN Q=P
660 !!TAB26"PARABOLIC FIT BY ";$4.03Q
665 !!"ANALYTE";TAB12"PARABOLIC COEFFICIENTS";
670 !" K1(y*y)+K2(y)+K3=x"
675 !TAB17"K1";TAB31"K2";TAB46"K3"
680 !TAB2$5.03An(Ii),
685 !Ka(Ii),Kb(Ii),Kc(Ii)
690 !!TAB4$4.03Q;TAB16"CONC.";TAB23"CONC.(CALC.)";
695 !TAB3"DIFF.";TAB13"%DIFF."
700 J=J+1: FOR I=1 TO N: !$10.2V(I),$5.3U(I),
702 !$5.3F(I),$5.3G(I),$5.2H(I): NEXT
705 IF J=2 THEN 755
710 !!TAB27"LINEAR FIT BY ";$4.03Q
715 !!"ANALYTE";TAB15"SLOPE";TAB28"INTERCEPT";
720 !TAB2"REGRESSION COEFF."
725 !TAB2$5.03An(Ii),
730 !Ks(Ii),Kh(Ii),Kf(Ii)
735 !!TAB4$4.03Q;TAB16"CONC.";TAB23"CONC.(CALC.)";
740 !TAB3"DIFF.";TAB13"%DIFF."
745 FOR I=1 TO N: F(I)=K(I): G(I)=L(I): H(I)=M(I): NEXT
750 GO TO 700
755 IF Z=2 THEN 760
756 Ki(Ii)=Ka(Ii): KJ(Ii)=Kb(Ii): Kk(Ii)=Kc(Ii)
757 Kl(Ii)=Kd(Ii): Km(Ii)=Ke(Ii): Kn(Ii)=Ks(Ii)
758 Ko(Ii)=Kh(Ii): Kw(Ii)=Ks(Ii): Ky(Ii)=Ku(Ii)
759 Z=2: GO TO 530
760 !!TAB6"ARITHMETIC MEAN";TAB37"GEOMETRIC MEAN"
762 !!TAB4"CONC.",TAB19"AREA",TAB34"CONC.",TAB49"AREA"
765 !!Kr(Ii),Kw(Ii),Kt(Ii),Ky(Ii)
770 !!TAB4"CONC.",TAB20"HT",TAB34"CONC.",TAB50"HT"
775 !!Kr(Ii),Ks(Ii),Kt(Ii),Ku(Ii)
780 !!"ENTER NEXT SET OF DATA LINES": END
800 DATA
810 DATA
820 DATA
```

PARABOLIC FIT BY AREA

ANALYTE	PARABOLIC COEFFICIENTS K1(y*y)+K2(y)+K3=x		
	K1	K2	K3
Cl-	-.1621-11	0.5169†-05	-.005474

AREA	CONC.	CONC.(CALC.)	DIFF.	%DIFF.
40412.	0.2	0.2	0.	0.4
80070.	0.4	0.4	-.	-.5
122126.	0.6	0.6	0.	0.3
164278.	0.8	0.8	-.	-.
208096.	1.	1.	-.	-.

LINEAR FIT BY AREA

ANALYTE	SLOPE	INTERCEPT	REGRESSION COEFF.
Cl-	209788.	-2876.4	0.9998487

AREA	CONC.	CONC.(CALC.)	DIFF.	%DIFF.
40412.	0.2	0.21	0.01	3.2
80070.	0.4	0.4	-.	-1.1
122126.	0.6	0.6	-.	-.7
164278.	0.8	0.8	-.	-.4
208096.	1.	1.01	0.01	0.6

PARABOLIC FIT BY HT

ANALYTE	PARABOLIC COEFFICIENTS K1(y*y)+K2(y)+K3=x		
	K1	K2	K3
Cl-	-.644†-09	0.0001225	0.0008211

HT	CONC.	CONC.(CALC.)	DIFF.	%DIFF.
1653.3	0.2	0.2	0.	0.0
3288.	0.4	0.4	-.	-.0
5029.3	0.6	0.6	0.	0.1
6784.	0.8	0.8	0.	0.3
8528.	1.	1.	-.	-.1

LINEAR FIT BY HT

ANALYTE	SLOPE	INTERCEPT	REGRESSION COEFF.
Cl-	8622.7	-117.10001	0.9999111

HT	CONC.	CONC.(CALC.)	DIFF.	%DIFF.
1653.3	0.2	0.21	0.01	2.7
3288.	0.4	0.39	-.01	-1.3
5029.3	0.6	0.6	-.	-.5
6784.	0.8	0.8	0.	0.
8528.	1.	1.	0.	0.3

Figure 5. Example of computer output from program "AUTPART2"

Table 4.--Listing of program"AUTPART3"

```
822 REM 'AUTPART3'
825 REM THE THIRD PART OF THIS PROGRAM CALCULATES THE
830 REM CONCENTRATION OF EACH ANALYTE IN EACH SAMPLE.
835 REM THE INDIVIDUAL ANALYTE'S CONCENTRATION MAY BE
840 REM CALCULATED USING EITHER A LINEAR OR NONLINEAR
845 REM FIT. CONCENTRATION IS CALCULATED BASED ON BOTH
850 REM AREA AND HEIGHT. IF THE AREA BASED CONCENTRATION
855 REM IS MORE THEN 10% GRATER THEN THE HEIGHT BASED
860 REM CONCENTRATION, A FLAG IS PRINTED.(**) SUCH PEAKS
865 REM SHOULD BE CHECKED FOR UNRESOLVED INTERFERRING
870 REM PEAKS.
880 REM BEFORE RUNNING THIS PROGRAM, THREE DATA LINES
885 REM MUST BE ENTERED.
895 REM THE FIRST DATA LINE HAS A FIVE CHARACTER
900 REM DISCRIPTION OF THE CONCENTRATION UNITS,
905 REM FOLLOWED BY AN INTEGER FOR EACH ANALYTE. A ONE
910 REM IS FOR A LINEAR FIT. A TWO FOR A PARABOLIC FIT.
915 REM THE SECOND DATA LINE HAS A SAMPLE I.D. AND THE
920 REM PEAK NUMBERS CORRESPONDING TO EACH ANALYTE IN THE
925 REM SAMPLE. THE THIRD DATA LINE HAS THE MULTIPLYER AND
930 REM DIVISOR OF THE CALCULATED CONCENTRATION.
945 REM AN EXAMPLE OF THE DATA LINES IS:
950 REM 1200 DATA "mg/L", 2, 2, 1, 2
955 REM 1210 DATA 246551, 9, 10, 11, 12
960 REM 1220 DATA 100, 5
1015 REM AFTER THE DATA LINES ARE ENTERED, ENTER RUN 1050.
1050 RESTORE 1200: READ A: FOR I=1 TO Ii: READ F(I): NEXT
1055 RESTORE 1210: READ S: FOR I=1 TO Ii: READ P(I): NEXT
1058 RESTORE 1220: READ B: READ C: FOR I=1 TO Ii:
1060 V(I)=Pa(P(I))/Af(I): W(I)=Ph(P(I))/Hf(I)
1065 IF F(I)=2 THEN 1080
1070 T(I)=Kl(I)*V(I)+Km(I): U(I)=Kd(I)*W(I)+Ke(I)
1075 GO TO 1090
```

Table 4.--(Continued)

```
1080 T(I)=Ki(I)*V(I)*V(I)+KJ(I)*V(I)+Kk(I)
1085 U(I)=Ka(I)*W(I)*W(I)+Kb(I)*W(I)+Kc(I)
1090 T(I)=T(I)*B/C: U(I)=U(I)*B/C: M(I)=0
1095 Z(I)=T(I)-U(I): Q(I)=100*Z(I)/U(I): Q(I)=ABS Q(I)
1100 IF Q(I)>10 THEN M(I)=1
1105 NEXT
1115 !TAB5"SAMPLE I.D.";$7S;TAB28"CONCENTRATION IN ";$5.03A;
1118 !TAB5"MULTIPLYER";$3B;"/";$3C
1120 !!"ANALYTE";TAB9"FIT";TAB14"PEAK#";TAB25"AREA";
1125 !TAB9"CONC.";TAB22"CONC.";TAB37"HT"
1130 FOR I=1 TO I1
1135 !TAB2$5.03An(I);TAB9$1F(I);TAB13$3P(I);
1140 !TAB4$10.2V(I),$7.4T(I);
1145 IF M(I)=1 THEN 1155
1150 !TAB6$7.4U(I),TAB17$10.2W(I): GO TO 1160
1155 !TAB2"**";TAB6$7.4U(I);TAB17$10.2W(I)
1160 NEXT : END
1200 DATA
1210 DATA
1220 DATA
```

Table 5.--Listing of program "AUTPART4"

```
1300 REM 'AUTPART4'
1302 REM THE FOURTH PART OF THIS PROGRAM CALCULATES
1304 REM THE MINIMUM CONCENTRATION, ABOVE WHICH A
1306 REM GIVEN RELATIVE ERROR MAY BE EXPECTED. THE
1308 REM PROGRAM CALCULATES THE EXPECTED VARIATION OF
1310 REM THE SLOPE OF THE CALIBRATION CURVE ASSUMING
1312 REM A STUDENT'S t DISTRIBUTION OF SLOPES OF LINES
1314 REM DRAWN FROM EACH DATA POINT TO THE ARITHMETIC
1316 REM OR GEOMETRIC MEAN. DATA POINTS WITHIN 10% OF
1318 REM THE CHOSEN MEAN ARE NOT USED.
1320 REM
1322 REM BEFOR RUNNING THIS PROGRAM, FOUR DATA LINES
1324 REM MUST BE ENTERED.
1326 REM THE FIRST DATA LINE HAS A FIVE CHARACTER
1328 REM DISCRIPTION OF THE ANALYTE, FOLLOWED BY THE
1330 REM NUMBER OF DATA POINTS.
1332 REM THE SECOND DATA LINE HAS THE CONC. DATA.
1334 REM THE THIRD LINE HAS A PEAK NUMBER
1336 REM CORRESPONDING TO THE HT OR AREA DATA.
1338 REM THE FOURTH DATA LINE HAS AN INTEGER FOR
1340 REM AREA (1) OR HT (2). AN INTEGER FOR
1342 REM ARITHMETIC (1) OR GEOMETRIC (2) MEAN,
1344 REM AND A CONFIDENCE LEVEL OF 90, 95, 98
1346 REM OR 99 PERCENT.
1356 REM AN EXAMPLE OF THE DATA LINES IS:
1358 REM 1800 DATA "Cl-", 5
1360 REM 1810 DATA .2, .4, .6, .8, 1
1362 REM 1820 DATA 2, 32, 62, 92, 112
1364 REM 1830 DATA 2, 1, 95
1400 RESTORE 1800: READ A: READ N
1405 RESTORE 1810: FOR I=1 TO N: READ U(I): NEXT
1410 RESTORE 1830: READ B: READ C: READ K
1415 IJ=Ii: FOR I=1 TO IJ: IF A=An(I) THEN Ii=I ALWAYS NEXT
1420 RESTORE 1820: FOR I=1 TO N: READ J
1440 IF B-1 THEN 1455
1445 V(I)=Pa(J)/Af(Ii): D=Kr(Ii): E=Kn(Ii)
1450 F=Kt(Ii): G=Ks(Ii): NEXT : GO TO 1470
1455 V(I)=Ph(J)/Hf(Ii): D=Kr(Ii): E=Ks(Ii)
1460 F=Kt(Ii): G=Ku(Ii): NEXT
1470 IF C-1 THEN D=F: E=G
1475 REM REJECT DATA POINTS WITHIN 10% OF MEAN CONC.
```

Table 5.--(Continued)

```
1480 O=H(I)*100/U(I): IF O<10 THEN U(I)=-1 ALWAYS NEXT
1485 FOR I=1 TO N: IF U(I)=-1 THEN NEXT
1490 J=J+1: X(J)=U(I): Y(J)=V(I): NEXT
1500 FOR I=1 TO J: U(I)=O-X(I): U(I)=ABS U(I)
1505 V(I)=E-V(I): V(I)=ABS V(I): H(I)=V(I)/U(I): NEXT
1510 O=0: P=0: FOR I=1 TO J: O=O+H(I): P=P+H(I)*H(I)
1515 NEXT : O=O*O/J: R=(P-O)/(J-1): S=SQR R
1520 N=0: C=" HT ": IF B-2 THEN C="AREA"
1525 IF B-2 THEN Z=Kn(Ii): W=Ko(Ii): GO TO 1535
1530 Z=Ks(Ii): W=Kh(Ii)
1535 GOSUB 1655
1537 M=T(J-1)*S/SQR (J-1)
1538 GOSUB 1610
1539 A=10: B=9.9
1540 F=Z+M: G=Z-M: H=E-(F*O): O=E-(G*O)
1545 N=N+1: M=E: L=0: I=0
1550 I=I+1: P=(M-L)/2+L: Q=(P-O)/G: R=(P-H)/F
1555 U=(P-W)/Z: S=U-Q: K=R-U
1560 IF S>K THEN V=S*100/U: GO TO 1570
1565 V=K*100/U
1570 IF V-A<0 THEN 1580 ELSE L=P: GO TO 1590
1580 IF V-B>0 THEN 1605 ELSE M=P
1589 REM SET I IN 1590 FOR MAXIMUM NUMBER OF ITERATIONS.
1590 IF I-50 THEN 1550
1600 !"50 ITERATIONS EXCEEDED": N=2: GO TO 1640
1605 IF N=2 THEN 1645 ELSE 1640
1610 !!TAB18"ERROR ANALYSIS OF "$5.03An(Ii)" CURVE"
1615 !!TAB3"DATA POINTS USED"
1618 !!TAB2"CONC.";TAB19$4.03C
1620 FOR I=1 TO J: !K(I),Y(I): NEXT
1625 !!TAB4"MEAN";TAB17"STANDARD";TAB34"MEAN";TAB49"MEAN"
1628 !TAB3"SLOPE";TAB16"DEVIATION";TAB33"CONC.";TAB48$4.03C
1630 !!O/O,S,O,E
1631 !
1632 !!TAB2"DEGREES";TAB14"STUDENT'S t";TAB32"CONFIDENCE"
1635 !TAB1"FREEDOM";TAB13"COEFFICIENT";TAB31"LEVEL"
1638 !!J-1,T(J-1),K: RETURN
1640 !!!" +- % ERROR";TAB17"MIN. CONC."
1645 !!V,U: IF N=2 THEN Ii=IJ: END
1650 A=100: B=99.9: GO TO 1545
1655 IF K=90 THEN 1730
1656 IF K=95 THEN 1720
```

Table 5.--(Continued)

```
1657 IF K=98 THEN 1710
1700 T(1)=63.657: T(2)=9.925: T(3)=5.841
1702 T(4)=4.604: T(5)=4.032
1705 T(6)=3.707: T(7)=3.499: T(8)=3.355
1708 T(9)=3.250: T(10)=3.169: RETURN
1710 T(1)=31.821: T(2)=6.965: T(3)=4.541
1712 T(4)=3.747: T(5)=3.365
1715 T(6)=3.143: T(7)=2.998: T(8)=2.896
1718 T(9)=2.821: T(10)=2.764: RETURN
1720 T(1)=12.706: T(2)=4.303: T(3)=3.182
1722 T(4)=2.776: T(5)=2.571
1725 T(6)=2.447: T(7)=2.365: T(8)=2.306
1728 T(9)=2.262: T(10)=2.228: RETURN
1730 T(1)=6.314: T(2)=2.92: T(3)=2.353
1732 T(4)=2.132: T(5)=2.015
1735 T(6)=1.943: T(7)=1.895: T(8)=1.86
1738 T(9)=1.833: T(10)=1.812: RETURN
1800 DATA
1810 DATA
1820 DATA
1830 DATA
```

Table 6.--Calculated "expected limit of detection" and "expected limit of quantitation" for six anions

mg/L = milligrams per liter; F^- = fluoride; Cl^- = chloride; PO_4^{-3} = orthophosphate; Br^- = bromide, NO_3^- = nitrate, SO_4^{-2} = sulfate

Constituent	Expected limit of detection (mg/L)	Expected limit of quantitation (mg/L)
F^-	0.012	0.086
Cl^-	.018	.140
PO_4^{-3}	.045	.264
Br^-	.015	.124
NO_3^-	.037	.240
SO_4^{-2}	.068	.336

Using the Software

Because the integrator has limited storage capacity, each of the programs above must be removed (scratched) from the integrator's memory before another program is loaded from the cassette recorder. For the same reason, an uncommented version of the programs must be used for actual calculations.

DISCUSSION

Suppressor induced variations in detector response

A set of five chloride standards containing 0.2, 0.4, 0.6, 0.8, and 1 mg/L chloride were analyzed in order of increasing concentration. Each standard was analyzed only once, but they were analyzed at intervals so that the resulting calibration curve was constructed over the entire stable lifetime of a suppressor column. The curve-fitting information generated by program "AUTPART2" from the five standards is shown in figure 5. Area and height fits are about equally as good, but the data can be fitted better to a second-order function than to a linear function.

A response factor for each of these chloride standards was calculated by dividing its corresponding peak height by its concentration. The difference between successive response factors as a function of suppressor exhaustion is shown in figure 6. Even after the suppressor was stabilized by exhausting about 20 percent of its capacity, the chloride response factor was still quite variable until about 50 percent exhaustion of the suppressor.

The origins of the detector-response variations over a suppressor's lifetime generally were attributed to interactions between the analyte's hydrogen-ion counter-ions and unsuppressed eluent or exchanged suppressor resin. A chemical origin was reasonable based on the fact that use of an internal standard did not improve the results obtained with calibration curves.

Interpretation of output from program "AUTPART2"

The fact that the five chloride standards previously discussed gave a calibration curve that fit a second-order function better than a linear function was a result of having analyzed the standards consecutively, from the standard of lowest concentration to the standard of highest concentration. The change in the chloride response factor as a function of suppresor exhaustion shown in figure 6, caused a change in the slope of the calibration curve. Standards placed randomly with respect to concentration, show a greater degree of linearity, and no significant difference in the precision of linear and parabolic fits.

The primary use of the parabolic fit information generated by program "AUTPART2" is to alert the analyst to a possible detector response versus time relationship. The absence of such a relationship insures variations in detector response over the suppressor's lifetime are reflected, without bias, in the least squares calibration line for each anion.

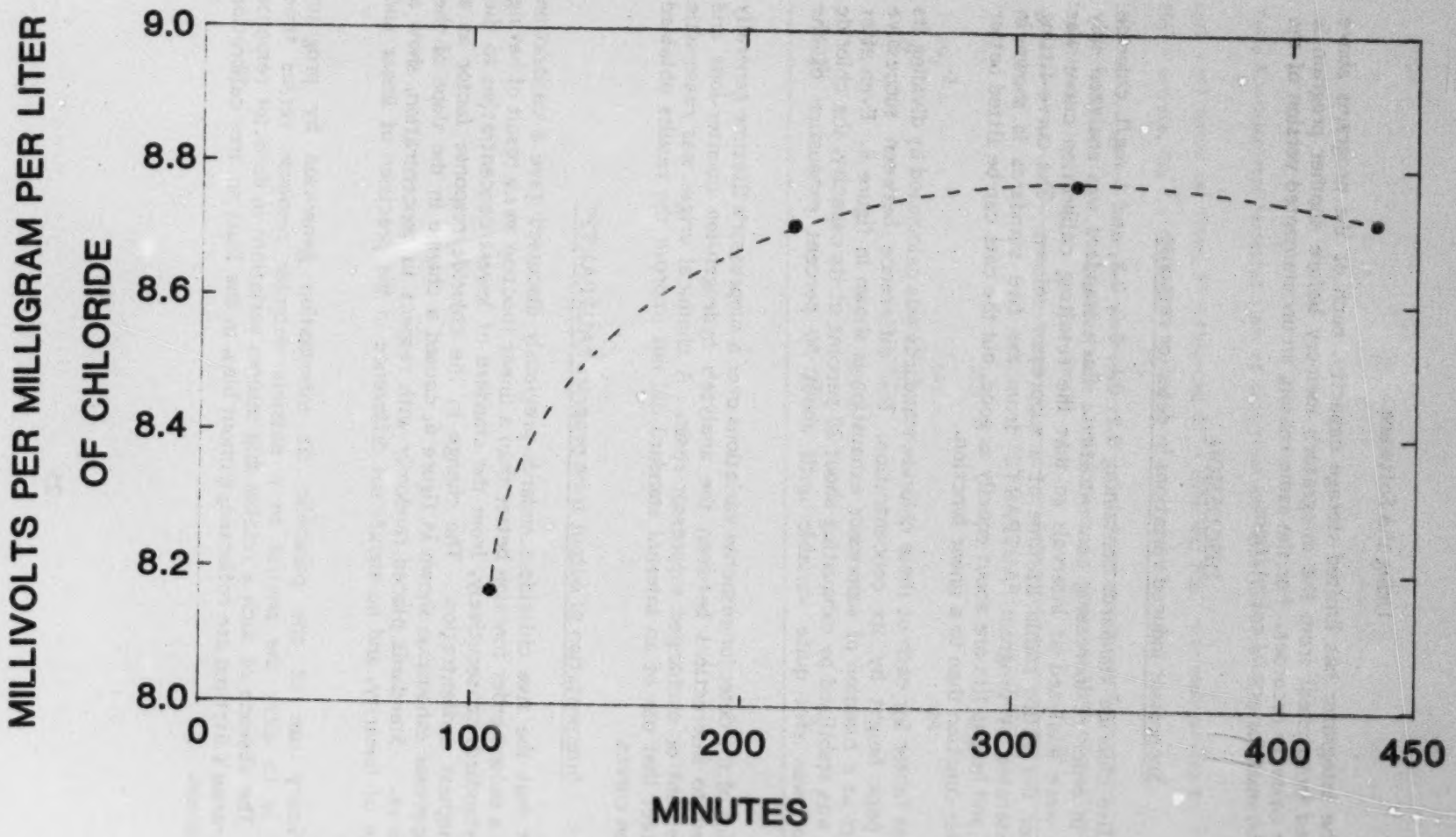

Figure 6. Variations in chloride response factor throughout the lifetime of a suppressor column.

Calibration curves based on peak height generally give better results than calculations based on peak area. The primary use of peak-area calculations is to detect interferences present as shoulders by comparing the peak-area and peak height results. Peak-area calculations can be useful when an analysis is conducted over a very stable, short part of the suppressor's lifetime, and the analyte of interest is present in very small concentrations.

Precision

The precision of this analytical method was determined by replicate analysis of six precipitation samples. Results were based on a linear peak-height concentration calibration curve, constructed over the stable lifetime of a suppressor column. The set of mixed standards used to construct the calibration curve for each anion were placed randomly in the sample tray with respect to concentration. This minimized any detector response time relationship in the detector response versus concentration data. The mean, standard deviation, and percent RSD (relative standard deviation) of the calculated concentration for each anion detected are shown in table 7.

The limit of detection of this method can probably be lowered by a factor of about 10, by exhausting the first 50 percent of the suppressor before beginning analysis. From 50 percent to complete exhaustion, the suppressor causes only minor variations in any anion's response factor, as shown for chloride in figure 6. Use of a short part of the suppressor's lifetime, during which the suppressor is at its maximum stability, should allow greater precision in quantitating anions using a calibration curve. Under these conditions, the specific-conductance cell's full scale setting can be decreased to 30 umho/cm. However, only about 5 h of useful analysis time is available.

Accuracy

To test the accuracy of this analytical system, five precipitation samples were spiked with two different concentration of anions, and the percent recovery calculated. The results are shown in table 8. The average recovery for all anions was 108 percent. The uniformly high recovery for all anions may be due to the inaccuracy of the addition of a small volume of concentrated eluent spike.

CONCLUSIONS

From the information and data presented, it is possible to design an automated analytical system for the ion-chromatographic determination of major anionic constituents in precipitation samples. Variations in detector response as a function of suppressor exhaustion is the major limiting factor in the precision of this method. A 50 percent exhausted suppressor could be used for analytical data requiring increased precision, when high sample throughput is not of great importance. Analytical accuracy is satisfactory. Percent recovery for all anions averaged 108 percent.

Table 7.--Analytical precision for six precipitation samples

mg/L = milligrams per liter; RSD = relative standard deviation; F^- = fluoride; Cl^- = chloride; PO_4^{-3} = orthophosphate; Br^- = bromide; NO_3^- = nitrate; SO_4^{-2} = sulfate; N.D. = not detected

Constituent	Sample	Replicates	Mean (mg/L)	Standard deviation	Percent RSD
F^-	1	20	0.023	0.005	22
Cl^-			1.94	.027	1
PO_4^{-3}			.686	.016	2
Br^-			N.D.	---	--
NO_3^-			1.40	.012	1
SO_4^{-2}			.381	.006	2
F^-	2	7	0.034	0.004	12
Cl^-			.305	.019	6
PO_4^{-3}			.510	.022	4
Br^-			N.D.	---	--
NO_3^-			.592	.019	3
SO_4^{-2}			.800	.015	2
F^-	3	7	0.025	0.003	12
Cl^-			.115	.012	10
PO_4^{-3}			N.D.	---	--
Br^-			N.D.	---	--
NO_3^-			.199	.018	9
SO_4^{-2}			.665	.011	2

Table 7.--Analytical precision for six precipitation samples (Continued)

Constituent	Sample	Replicates	Mean (mg/L)	Standard deviation	Percent RSD
F^-	4	7	0.042	0.005	12
Cl^-			.207	.015	7
PO_4^{-3}			N.D.	---	--
Br^-			N.D.	---	--
NO_3^-			.812	.017	2
SO_4^{-2}			1.096	.021	2
F^-	5	7	0.060	0.004	7
Cl^-			.388	.016	4
PO_4^{-3}			N.D.	---	--
Br^-			N.D.	---	--
NO_3^-			.280	.010	4
SO_4^{-2}			.776	.016	2
F^-	6	7	0.029	0.005	17
Cl^-			.341	.013	4
PO_4^{-3}			N.D.	---	--
Br^-			N.D.	---	--
NO_3^-			.861	.023	3
SO_4^{-2}			.750	.023	3

Table 8.--Analytical accuracy for five precipitation samples

mg/L = milligrams per liter; F^- = fluoride; Cl^- = chloride; PO_4^{-3} = orthophosphate; NO_3^- = nitrate; SO_4^{-2} = sulfate.

Constituent	Sample	Present (mg/L)	Added (mg/L)	Found (mg/L)	Percent recovery
F^-	2	0.034	0.018	0.055	106
F^-		.034	.036	.073	104
Cl^-		.305	.045	.378	108
Cl^-		.305	.091	.391	99
PO_4^{-3}		.510	.454	1.021	106
PO_4^{-3}		.510	.910	1.564	110
NO_3^-		.592	.182	.863	111
NO_3^-		.592	.364	1.017	106
SO_4^{-2}		.800	.182	1.086	110
SO_4^{-2}		.800	.364	1.271	109
F^-	3	0.025	0.018	0.046	107
F^-		.025	.036	.066	108
Cl^-		.115	.045	.183	114
Cl^-		.115	.091	.222	108
NO_3^-		.199	.182	.442	116
NO_3^-		.199	.364	.597	106
SO_4^{-2}		.665	.182	.952	112
SO_4^{-2}		.665	.364	1.191	116

Table 8.--Analytical accuracy for five precipitation samples (Continued)

Constituent	Sample	Present (mg/L)	Added (mg/L)	Found (mg/L)	Percent recovery
F^-	4	0.042	0.018	0.067	112
F^-		.042	.036	.086	110
Cl^-		.207	.045	.298	118
Cl^-		.207	.091	.336	113
NO_3^-		.812	.182	1.000	101
NO_3^-		.812	.364	1.212	103
SO_4^{-2}		1.096	.182	1.423	111
SO_4^{-2}		1.096	.364	1.599	110
F^-	5	0.060	0.018	0.079	101
F^-		.060	.036	.097	101
Cl^-		.388	.045	.468	108
Cl^-		.388	.091	.479	100
NO_3^-		.280	.182	.467	101
NO_3^-		.280	.364	.649	101
SO_4^{-2}		.776	.182	.965	101
SO_4^{-2}		.776	.364	1.146	100

Table 8.--Analytical accuracy for five precipitation samples (Continued)

Constituent	Sample	Present (mg/L)	Added (mg/L)	Found (mg/L)	Percent recovery
F^-	6	0.029	0.018	0.057	121
F^-		.029	.036	.074	114
Cl^-		.341	.045	.417	108
Cl^-		.341	.091	.444	103
NO_3^-		.861	.182	1.106	106
NO_3^-		.861	.364	1.298	106
SO_4^{-2}		.750	.182	1.006	108
SO_4^{-2}		.750	.364	1.186	106

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